

Analysis of the spin Hall effect in CuIr alloys: Combined approach of density functional theory and Hartree-Fock approximation

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We analyze the spin Hall effect in CuIr alloys in theory by the combined approach of the density functional theory (DFT) and Hartree-Fock (HF) approximation. The SHA is obtained to be negative without the local correlation effects. After including the local correlation effects of the $5d$ orbitals of Ir impurities, the SHA becomes positive with realistic correlation parameters, and consistent with experiment [Niimi et al., Phys. Rev. Lett. **106**, 126601 (2011)]. Moreover, our analysis shows that the DFT+HF approach is a convenient and general method to study the influence of local correlation effects on the spin Hall effect.

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I. INTRODUCTION

The spin Hall effect (SHE) converts charge current into spin current, which is crucial for the further development of spintronic devices. The key material parameter in a device based on this effect is the spin Hall angle (SHA): the ratio between the induced spin Hall current and the input charge current. If the sign of SHA changes, the direction of the induced spin Hall current is also reversed. In the experiment on CuIr alloys, the dominant contribution to the SHE was verified to be by an extrinsic skew scattering mechanism and the SHA was measured to be positive 2.1% [1].

According to the skew scattering approach of Fert and Levy [2, 3], the phase shift of the $6p$ orbitals of Ir is decisive as to the sign of the SHA of CuIr. A positive SHA can be obtained as long as the phase shift of $6p$ has a small positive value [3], and our aim is to find a microscopic argument for this, rather than treating it as a free parameter. Other approaches based on the Boltzmann equation and Kubo-Streda formula even give negative values of SHA, (according to the definition of SHA from resistivities)[4], opposite to the experimental sign. Therefore, a clear and convenient theoretical approach which can reproduce and explain the sign of the SHA is still required.

In the present work, by the combined approach of the density functional theory (DFT) and Hartree-Fock (HF) approximation, we calculate the SHA including correlation effects, and find that the local correlation effects of the $5d$ orbitals of Ir give the sign of SHA consistent with experiment.

II. SKEW SCATTERING

For the CuIr alloys, the spin orbit interactions (SOI) in the $5d$ orbitals of the Ir impurities induce the extrinsic SHE. It has been observed in experiment that the spin

Hall resistivity increases linearly with the impurity concentration, so that the SHE is predominantly attributed to a skew scattering extrinsic contribution [1]. Thus, the nonmagnetic CuIr alloys can be described by a single-impurity multi-orbital Anderson model [5]:

$$\begin{aligned}
 H_{00} &= \sum_{\mathbf{k}, \alpha, \sigma} \epsilon_{\alpha \mathbf{k}} c_{\mathbf{k} \alpha \sigma}^\dagger c_{\mathbf{k} \alpha \sigma}, \\
 H_0 &= H_{00} + \sum_{\mathbf{k}, \alpha, \beta, \sigma} (V_{\beta \mathbf{k} \alpha} d_{\beta \sigma}^\dagger c_{\mathbf{k} \alpha \sigma} + \text{H.c.}) + \sum_{\beta, \sigma} \epsilon_{\beta} n_{\beta \sigma}, \\
 H_{SO} &= \frac{\lambda_p}{2} \sum_{\zeta \sigma, \zeta' \sigma'} d_{\zeta \sigma}^\dagger (\mathbf{l})_{\zeta \zeta'} \cdot (\boldsymbol{\sigma})_{\sigma \sigma'} d_{\zeta' \sigma'} \\
 &\quad + \frac{\lambda_d}{2} \sum_{\xi \sigma, \xi' \sigma'} d_{\xi \sigma}^\dagger (\mathbf{l})_{\xi \xi'} \cdot (\boldsymbol{\sigma})_{\sigma \sigma'} d_{\xi' \sigma'}, \\
 H &= H_0 + H_{SO} + U \sum_{\xi} n_{\xi \uparrow} n_{\xi \downarrow} \\
 &\quad + \frac{U'}{2} \sum_{\xi \neq \xi', \sigma, \sigma'} n_{\xi \sigma} n_{\xi' \sigma'} - \frac{J}{2} \sum_{\xi \neq \xi', \sigma} n_{\xi \sigma} n_{\xi' \sigma},
 \end{aligned} \tag{1}$$

where $\epsilon_{\alpha \mathbf{k}}$ is the energy band α of the host Cu, ϵ_{β} is the energy level of the orbital β of the impurity Ir, and $V_{\beta, \alpha}(\mathbf{k})$ is the hybridization between the orbital β of Ir and the band α of Cu. U (U') is the on-site Coulomb repulsion within (between) the $5d$ orbitals of Ir, and J is the Hund coupling between the $5d$ orbitals of Ir. The relations of $U = U' + 2J$ and $J/U = 0.3$ are kept [6]. The SOI is included in both the $6p$ orbitals ζ and the $5d$ orbitals ξ of Ir, with the parameters λ_p and λ_d , respectively. We include the on-site Coulomb interactions only within the $5d$ orbitals of Ir in Eq.(1), but not within the $6p$ orbitals, which are much more extended [7].

The SOI included in the d orbitals will split the d states with the orbital angular momentum l into the states of $d \pm$ with the total angular momentum $j = l \pm \frac{1}{2}$. The degeneracy of the $d+$ and $d-$ states is six and four, re-

spectively. For the $5d$ states with SOI of Ir, we have the relations of $n_{d+} = N_{d+}^{Ir}/6$ and $n_{d-} = N_{d-}^{Ir}/4$, where $n_{d\pm}$ are the occupation number of each of the degenerate states $5d\pm$, and $N_{d\pm}^{Ir}$ are the total occupation number of the $5d\pm$ states. The values of $n_{d\pm}$ will be between 0 and 1. The total occupation number of the $5d$ states of Ir $N_d^{Ir} = N_{d+}^{Ir} + N_{d-}^{Ir}$. Similarly, the SOI splits the p orbitals into $p\pm$ states.

Since a net charge cannot exist in metal, the total occupation numbers of the valence states of $6s$, $6p$ and $5d$ of Ir is conserved as [8]

$$N_s^{Ir} + N_p^{Ir} + N_d^{Ir} = 9, \quad (2)$$

where the occupation numbers are defined via projections of the occupied states onto the Wannier states centered at the Ir sites and extended in the whole supercell.

Following the method of Ref. [9] and the definition of SHA Θ in terms of resistivity ρ [8], the SHA of CuIr can be calculated from the phase shifts δ_1^\pm of the $p\pm$ and δ_2^\pm of the $d\pm$ channels as

$$\Theta(\delta_1^+, \delta_1^-, \delta_2^+, \delta_2^-) = A/B,$$

$$A = -2[9 \sin(\delta_1^+ - \delta_2^+) \sin \delta_1^+ \sin \delta_2^+ \\ - 4 \sin(\delta_1^+ - \delta_2^-) \sin \delta_1^+ \sin \delta_2^- \\ - 5 \sin(\delta_1^- - \delta_2^-) \sin \delta_1^- \sin \delta_2^-],$$

$$B = 45 \sin^2 \delta_2^+ + 30 \sin^2 \delta_2^- + 50 \sin^2 \delta_1^+ + 25 \sin^2 \delta_1^- \\ + 6 \sin \delta_1^+ \sin(2\delta_2^+ - \delta_1^+) + 12 \sin \delta_1^- \sin(2\delta_2^+ - \delta_1^-) \\ + 14 \sin \delta_1^+ \sin(2\delta_2^- - \delta_1^+) - 2 \sin \delta_1^- \sin(2\delta_2^- - \delta_1^-). \quad (3)$$

The phase shifts can be obtained by the Friedel sum rule [2, 10]:

$$\delta_\mu^\pm = \pi(N_{\mu\pm}^{Ir} - N_{\mu\pm}^{Cu})/D_{\mu\pm}, \quad (4)$$

where $\mu=1$ for p orbitals with the degeneracies $D_{1+}=4$ and $D_{1-}=2$, $\mu=2$ for d orbitals with $D_{2+}=6$ and $D_{2-}=4$.

III. DFT RESULTS

For the DFT calculation, we employ the code of Quantum Espresso (QE) [12]. We use a primitive cell of a single Cu atom to calculate the H_{00} exclusively for the case of pure Cu, and a supercell of Cu_{26}Ir to calculate the H_0 for the case of CuIr alloys. The cutoff energy of planewaves is 50 Ry. The pseudopotentials are ultrasoft for calculations without SOI and projector-augmented-wave for calculations with SOI. The type of exchange-correlation functionals is PBE [13]. The energy convergence limit is 10^{-8} Ry. The k lattice is $8 \times 8 \times 8$.

By the DFT calculations of H_{00} and H_0 in Eq.(1) for pure Cu and CuIr, respectively, the occupation numbers of $4s$, $4p$, $3d$ states of Cu and $6s$, $6p$, $5d$ states of Ir are obtained to be $N_s^{Cu}=0.35$, $N_p^{Cu}=0.96$, $N_d^{Cu}=9.68$ and $N_s^{Ir}=0.32$, $N_p^{Ir}=0.86$, $N_d^{Ir}=7.82$, respectively. Thus the

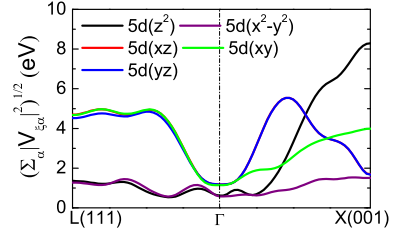


FIG. 1. The hybridization function between the $5d$ orbitals of the Ir impurity and the bulk Cu host.

total occupation number $N_s^{Ir} + N_p^{Ir} + N_d^{Ir} = 9.0$, confirming the relation in Eq.(2). Including the SOI, the DFT calculations for pure Cu and CuIr give the phase shifts of $\delta_1^+ = -0.09$, $\delta_1^- = 0.06$, $\delta_2^+ = -0.73$ and $\delta_2^- = -0.38$, by Eq.(4). The SHA is obtained to be -2.7% by Eq.(3), which is close to the prediction in Ref. [11], but is inconsistent with the positive sign in experiment [1].

IV. DFT+HF APPROACH

The hybridization between the $5d$ orbitals of the Ir impurity and the Cu host is defined as

$$V_{\xi\mathbf{k}\alpha} \equiv \langle \varphi_\xi | H_0 | \Psi_\alpha(\mathbf{k}) \rangle, \quad (5)$$

where φ_ξ is the Ir impurity state in real space with the $5d$ orbital index ξ , and $\Psi_\alpha(\mathbf{k})$ is the Cu host state in k -space with the band index α and wavevector \mathbf{k} . Following the method in Ref. [14], and using the post-processor code Wannier90 [15], $V_{\xi\mathbf{k}\alpha}$ were obtained. In Fig. 1 we plot the function $(\sum_\alpha |V_{\xi\mathbf{k}\alpha}|^2)^{1/2}$.

Based on the Anderson model [5], the $5d$ states of Ir impurities are considered as virtual bound states with width Δ . Including correlation U on the virtual bound states, the impurity level increases while the occupation number decreases, as shown schematically in Fig. 2. Taking the results of $V_{\xi\mathbf{k}\alpha}$ by Eq.(5), the width parameter Δ_ξ of the virtual bound state for each $5d$ orbital ξ of Ir is obtained by the relation [5]

$$\Delta_\xi = \pi \sum_{\alpha, \mathbf{k}} \delta(\epsilon_F - \epsilon_{\alpha\mathbf{k}}) |V_{\xi\mathbf{k}\alpha}|^2, \quad (6)$$

where ϵ_F is the Fermi level. As a result, the width Δ for the whole $5d$ orbitals of Ir is the average of each Δ_ξ , $\Delta = (\sum_\xi \Delta_\xi)/5 = 1.76$ eV.

Based on the Anderson model of $H_0 + H_{SO}$ in Eq.(1), for the nonmagnetic CuIr including SOI but without correlation U , there are self-consistent relations between the spin-orbit split states of $5d+$ and $5d-$ of Ir [5]:

$$\Delta \cot(\pi n_{d\pm}) = E_{0,d\pm}, \quad (7)$$

where the $5d\pm$ states of Ir under $U=0$ has the energy level of $E_{0,d\pm}$. The DFT results of $H_0 + H_{SO}$ in Eq.(1) give

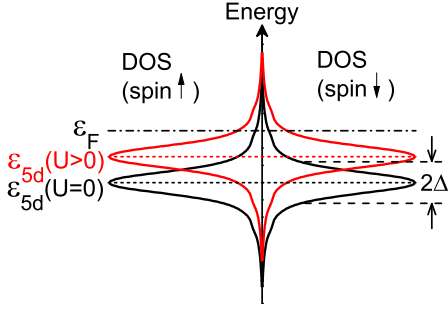


FIG. 2. Schematic picture of the density of states (DOS) of the 5d virtual bound states with width Δ of Ir in the nonmagnetic CuIr alloys, with the on-site Coulomb repulsion $U=0$ (black) and $U>0$ (red), respectively. ε_{5d} is the impurity level in the Hartree-Fock approximation which will increase with U , and ε_F is the Fermi level.

$n_{d+}=0.734$ and $n_{d-}=0.849$. Then Eq.(7) gives $E_{0,d+}=-1.59$ eV and $E_{0,d-}=-3.43$ eV.

For correlation $U > 0$, based on Eq.(1) with HF approximation, the self-consistent relations are rewritten as

$$\begin{aligned} E_{d\pm} &= \Delta \cot(\pi n_{d\pm}) \\ &= E_{0,d\pm} + U\left(\frac{3}{5}n_{d+} + \frac{2}{5}n_{d-}\right) + U'\left(\frac{24}{5}n_{d+} + \frac{16}{5}n_{d-}\right) \\ &\quad - J\left(\frac{12}{5}n_{d+} + \frac{8}{5}n_{d-}\right), \end{aligned} \quad (8)$$

from which the n_{d+} and n_{d-} can be obtained for each positive U . Eq.(8) directly includes all the five 5d orbitals of Ir, as well as the local correlations, and the calculation is self-consistent.

As U increases from 0, the occupation number $N_d^{Ir} = 6n_{d+} + 4n_{d-}$ decreases, as shown in Fig. 3(a). The phase shifts δ_2^{\pm} obtained by Eq.(4) are plotted in Fig. 3(b). The ratios of $N_p^{Ir}/N_s^{Ir}=2.7$ and $N_{p+}^{Ir}/N_{p-}^{Ir}=1.4$ from DFT with $U=0$, and the relation in Eq.(2) are taken to evaluate the occupation numbers $N_{p(\pm)}^{Ir}$. The phase shifts δ_1^{\pm} obtained from Eq.(4) are shown in Fig. 3(c). Finally, the SHA $\Theta(\delta_1^+, \delta_1^-, \delta_2^+, \delta_2^-)$, calculated from Eq.(3), is shown in Fig. 3(d). In order to compare the contributions from the p and d orbitals separately, we consider the two limiting cases of $\delta_1^+ = \delta_1^- = \delta_1$ and $\delta_2^+ = \delta_2^- = \delta_2$. We define δ_1 and δ_2 from Eq.(4) with the total occupation numbers of each orbital and the degeneracies 6 and 10 respectively, and plot them in Figs. 3(c) and (b). The SHA of the two limiting cases $\Theta(\delta_1, \delta_1, \delta_2^+, \delta_2^-)$ and $\Theta(\delta_1^+, \delta_1^-, \delta_2, \delta_2)$ are plotted in Figs. 3(d).

In addition, we need to evaluate the range of U within which the nonmagnetic state of CuIr is the ground state. Following Anderson's method to calculate the critical value of U between nonmagnetic and magnetic states [5], neglecting the SOI as an approximation, based on the $H - H_{SO}$ in Eq.(1), there are self-consistent relations

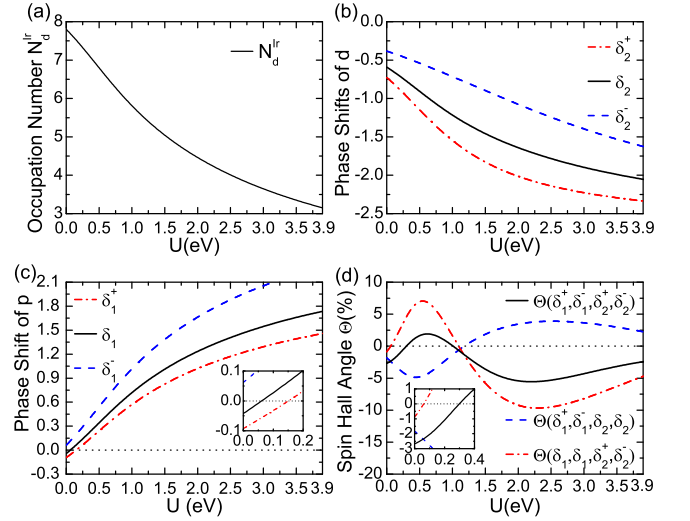


FIG. 3. (a) The occupation number of the 5d orbitals of Ir N_d^{Ir} , (b) the phase shifts obtained by Eq.(4) of d orbitals with SOI (δ_2^{\pm}) and without SOI (δ_2), (c) p orbitals with SOI (δ_1^{\pm}) and without SOI (δ_1), and (d) the SHA Θ as functions of correlation U . The inserts show the details around $U=0$.

among the five degenerate 5d orbitals:

$$\begin{aligned} E_{\xi,\sigma} &= \Delta \cot(\pi n_{\xi,\sigma}) \\ &= E_0 + U n_{\xi,-\sigma} + U' \sum_{\xi' \neq \xi} (n_{\xi',\sigma} + n_{\xi',-\sigma}) \\ &\quad - J \sum_{\xi' \neq \xi} n_{\xi',\sigma}, \end{aligned} \quad (9)$$

For the nonmagnetic case, $n_{\xi,\uparrow} = n_{\xi,\downarrow} = n$, we have

$$\Delta \cot(\pi n) = E_0 + U n + 8U' n - 4J n. \quad (10)$$

Taking the parameters of $n=0.78$ obtained from the DFT calculation of H_0 in Eq.(1) and $\Delta=1.76$ eV obtained from Eq.(5), Eq.(10) gives $E_0 = \Delta \cot(\pi n) = -2.16$ eV.

For the magnetic case, by differentiating Eq.(9),

$$\begin{aligned} -\frac{\Delta\pi}{\sin^2 \pi n} \delta n_{\xi,\sigma} &= U \delta n_{\xi,-\sigma} + U' \sum_{\xi' \neq \xi} (\delta n_{\xi',\sigma} + \delta n_{\xi',-\sigma}) \\ &\quad - J \sum_{\xi' \neq \xi} \delta n_{\xi',\sigma}. \end{aligned} \quad (11)$$

Letting $\delta n_{\sigma} = \sum_{\xi} \delta n_{\xi,\sigma}$, from Eq.(11)

$$-\frac{\Delta\pi}{\sin^2 \pi n} \delta n_{\sigma} = U \delta n_{-\sigma} + U' (4\delta n_{\sigma} + 4\delta n_{-\sigma}) - 4J \delta n_{\sigma}, \quad (12)$$

$$\frac{\Delta\pi}{\sin^2 \pi n} (\delta n_{\uparrow} - \delta n_{\downarrow}) = (U + 4J) (\delta n_{\uparrow} - \delta n_{\downarrow}). \quad (13)$$

For the magnetic case, $\delta n_{\uparrow} - \delta n_{\downarrow} \neq 0$, thus

$$\frac{\Delta\pi}{\sin^2 \pi n} = U + 4J. \quad (14)$$

With the parameters of $\Delta=1.76$ eV and $E_0=-2.16$ eV already obtained above, and the fixed relations of $U' = U - 2J$ and $J = 0.3U$ [6, 8], by solving Eqs.(10) and (14) simultaneously, it gives the critical occupation number n_c and the critical correlation parameter U_c between the nonmagnetic phase and magnetic phase to be $n_c=0.30$ and $U_c=3.92$ eV. The critical value of the total occupation number $(N_d^{Ir})_c = 10n_c=3.0$. Thus the results in Fig. 3 are of the nonmagnetic states. As the correlation U increases from zero up to the nonmagnetic limit of 3.92 eV, the SHA is non-monotonic.

V. ANALYSIS OF THE SPIN HALL EFFECT

As shown in Fig. 3(a), as the correlation U on the $5d$ orbitals of Ir increases from 0, N_d^{Ir} decreases, which is consistent with the picture from the Anderson model [5] as in Fig. 2. Due to the relation in Eq.(2), the decrease of N_d^{Ir} is accompanied by the increase of N_p^{Ir} . According to Eq.(4), the phase shifts δ_2 and δ_2^\pm decrease, while δ_1 and δ_1^+ increase from negative to positive, and δ_1^- is always positive and increases in magnitude, as shown in Fig. 3(b) and (c).

From Fig. 3(d), we note that at $U=0$, the magnitude of the calculated SHA $\Theta(\delta_1^+, \delta_1^-, \delta_2, \delta_2)$ with SOI only in the p orbitals is larger than $\Theta(\delta_1, \delta_1, \delta_2^+, \delta_2^-)$, with SOI only in the d orbitals. This is consistent with the results in Ref.[16]. As the correlation U increases to a realistic value for Ir of around 0.5 eV [17], the SHA including SOI in both p and d orbitals, $\Theta(\delta_1^+, \delta_1^-, \delta_2^+, \delta_2^-)$, goes from negative to positive values. At $U=0.5$ eV, the SHA is

+1.6%, quite close to the experimental value of +2.1% [1]. If the SOI is included only in the $5d$ orbitals of Ir, the resulting SHA $\Theta(\delta_1, \delta_1, \delta_2^+, \delta_2^-)$ still qualitatively follows the complete function $\Theta(\delta_1^+, \delta_1^-, \delta_2^+, \delta_2^-)$. If, on the other hand, we consider the SOI only in the p orbitals, the predicted SHA $\Theta(\delta_1^+, \delta_1^-, \delta_2, \delta_2)$ around $U=0.5$ eV is opposite in sign to the experiment. This is because the relative magnitudes of $\Theta(\delta_1, \delta_1, \delta_2^+, \delta_2^-)$ and $\Theta(\delta_1^+, \delta_1^-, \delta_2, \delta_2)$ are reversed as U increases from 0 to the realistic value. In addition, the SOI of the more extended $6p$ orbitals of Ir is likely to be overestimated by the DFT calculation; thus the contribution due to the SOI in the p orbitals terms may be exaggerated. These results suggest the physical reason for the SHA of CuIr observed in experiment: it is the local correlation effects of the $5d$ orbitals of Ir which determine the sign of the SHA.

In conclusion, by the combined approach of DFT and HF approximation, we show that the local correlation effects of the $5d$ orbitals of Ir give the sign of the SHA consistent with experiment. This indicates it is a convenient and general method to study the influence of local correlations effects on the SHE, for various combinations of hosts and impurities and for a wide range of U .

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- [1] Y. Niimi, M. Morota, D. H. Wei, C. Deranlot, M. Basletic, A. Hamzic, A. Fert, and Y. Otani, Phys. Rev. Lett. **106**, 126601 (2011).
 - [2] A. Fert, A. Friederich, and A. Hamzic, J. Magn. Magn. Mater. **24**, 231 (1981).
 - [3] A. Fert and P. M. Levy, Phys. Rev. Lett. **106**, 157208 (2011); Phys. Rev. Lett. **111**, 199904 (2013).
 - [4] D. V. Fedorov, C. Herschbach, A. Johansson, S. Ostanin, I. Mertig, M. Gradhand, K. Chadova, D. Ködderitzsch, and H. Ebert, Phys. Rev. B **88**, 085116 (2013).
 - [5] P. W. Anderson, Phys. Rev. **124**, 41 (1961).
 - [6] S. Maekawa, T. Tohyama, S. E. Barnes, S. Ishihara, W. Koshibae and G. Khaliullin, *Physics of Transition Metal Oxides*, Springer, 2004.
 - [7] B. Gu, Z. Xu, M. Mori, T. Ziman, and S. Maekawa, arXiv:1402.3012 (unpublished).
 - [8] Z. Xu, B. Gu, M. Mori, T. Ziman, and S. Maekawa, arXiv:1405.7449 (unpublished).
 - [9] G. Y. Guo, S. Maekawa, and N. Nagaosa, Phys. Rev. Lett. **102**, 036401 (2009).
 - [10] D. C. Langreth, Phys. Rev. **150**, 516 (1966).
 - [11] A. Johansson, C. Herschbach, D. V. Fedorov, M. Gradhand, and I. Mertig, J. Phys.: Condens. Matter **26**, 274207 (2014).
 - [12] P. Giannozzi et al., <http://www.quantum-espresso.org>.
 - [13] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
 - [14] B. Gu, J.-Y. Gan, N. Bulut, G.-Y. Guo, N. Nagaosa, and S. Maekawa, J. Phys. Conf. Ser. **200**, 062007 (2010).
 - [15] A. A. Mostofi et al., Comput. Phys. Commun., **178**, 685 (2008).
 - [16] C. Herschbach, D. V. Fedorov, I. Mertig, M. Gradhand, K. Chadova, H. Ebert, and D. Ködderitzsch, Phys. Rev. B **88**, 205102 (2013).
 - [17] S. J. Moon, H. Jin, K.W. Kim, W. S. Choi, Y. S. Lee, J. Yu, G. Cao, A. Sumi, H. Funakubo, C. Bernhard, and T.W. Noh, Phys. Rev. Lett. **101**, 226402 (2008).